



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : B05D 1/00, C08F 6/06 C08J 3/12, C09D 167/02</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 94/09913</b> (43) International Publication Date: 11 May 1994 (11.05.94)</p>
<p>(21) International Application Number: PCT/US93/10289 (22) International Filing Date: 27 October 1993 (27.10.93) (30) Priority data: 07/970,401 2 November 1992 (02.11.92) US (71) Applicant: THE FERRO CORPORATION [US/US]; 1000 Lakeside Avenue, Cleveland, OH 44114-1183 (US). (72) Inventors: MANDEL, Frederick, S. ; 16532 Haskins Road, Chagrin Falls, OH 44022 (US). GREEN, Charles, D. ; 2354 Olde Farm Lane, Hudson, OH 44236 (US). SCHEIBELHOFFER, Anthony, S. ; 2986 Wilbanks Drive, Norton, OH 44203 (US).</p>	<p>(74) Agent: CLARK, Kenneth, A.; Rankin, Hudak &amp; Hill, 925 Euclid Avenue, Suite 600, Cleveland, OH 44115 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, PL, RO, RU, SD, SE, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). <b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: METHOD OF PREPARING COATING MATERIALS</p> <p>(57) Abstract</p> <p>The present invention provides a new and improved method of producing coating materials comprising the steps of providing a first organic material which is solid at room temperature, providing a second organic material which is solid at room temperature and which is substantially different in chemical composition from the first organic material, providing a source of supercritical fluid (16), providing a first container (12) having a mechanical agitator (52), providing a second container (14), introducing the first and second organic materials and the supercritical fluid into the first container and mechanically agitating such materials and the supercritical fluid, and discharging the contents of the first container (12) into the second container (14) so as to collect substantially all of the first and second organic materials in the second vessel, the second container being maintained at a lower pressure than the first container.</p>		

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Title: METHOD OF PREPARING COATING MATERIALS

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Technical Field

This invention concerns coating materials and specifically coating powders. These coating powders are utilized to impart a decorative and/or functional coating or finish to objects of manufacture. More particularly, the invention concerns a new and improved method of utilizing a process media such as a supercritical fluid in the manufacture of coating powders.

Background

Coating powders (also known in the industry as powder coatings) are a mixture of fine particles that are utilized to provide a protective coating on an object. Such powders comprise a mixture of thermoplastic or thermosetting polymeric resin materials, pigments, cross-linking agents, catalysts, flow aids and other materials.

Currently, coating powders are generally used by applying such powders to the object being coated using electrostatic powder spray or fluidized bed coating equipment. In the electrostatic process, the coating powder is dispersed in an airstream and passed through a high voltage field where the particles pick up an electrostatic charge. The charged particles are attracted to and deposited on the object to be coated which is usually at room temperature. The object is

5        then placed in an oven where the powder melts, cures and forms  
a coating on the object. In fluidized bed applications the  
object to be coated is heated to a temperature above the  
curing temperature of the coating powders. This heated object  
is then passed through an air fluidized cloud of the coating  
10        powders. The coating powders melt and cure as they come into  
contact with the hot object. Coating powders are generally  
utilized to produce coatings with film thicknesses of about .8  
to 50 mils.

Coating powders are generally produced by first dry  
15        mixing the various constituents that form the powder (e.g., a  
base resin, a curing agent, pigments, flow agents). This  
mixture is then fed into a suitable melt mixer such as a twin  
screw extruder which melt mixes the constituents at an  
elevated temperature (e.g., about 250-400°F). The molten  
20        mixture which is produced by the extruder is then cooled by  
use of chill rollers and mechanically flaked. Finally, the  
flaked material is milled in an air classification mill to an  
average particle size of about 20-50  $\mu$ m.

The conventional processing of coating powders does  
25        present some downsides. For example, the high temperature  
processing in the extruder can bring about the premature  
reaction of the curing agent or the degradation of the polymer  
resins. Additionally, the particles produced by the  
conventional method tend to vary greatly in size thereby  
30        requiring the use of various particle separation techniques  
such as screening and/or cyclone separation in order to  
separate undesirable large and small particles. Particles of  
undesirable size must then be downgraded or disposed of. The

5 conventional method can produce particles that do not display  
uniformity in composition. For example, some particles may  
contain excess pigment while other particles may contain too  
little pigment. The conventional process also presents a  
drawback in that there is a limit to the amount of raw  
10 materials that can be mixed at one time. More particularly,  
most conventional processing equipment can only handle about  
2000 pounds of material during the dry mixing operation.

#### Summary Of The Invention

15 The present invention provides a new and improved method  
of producing coating powders that affords various distinct  
advantages over prior art processing techniques. More  
particularly, the present inventive process produces particles  
of more uniform size and homogeneous composition. Also,  
during the process there is substantially no undesirable  
20 reaction of curing agents or degradation of the polymer resins  
since the process operates at lower temperatures. Accord-  
ingly, the invention allows the use of resins and curing  
agents that are not suitable for use in conventional extruder-  
type processes because of heat sensitivity. Additionally, it  
25 is contemplated that larger batch sizes, that are well in  
excess of conventional batch sizes, can be produced. Further,  
coating powders produced in accordance with the present  
invention exhibit particles that are more "spherical" in shape  
as compared to prior art coating powders. Spherical particles  
30 are generally preferred for electrostatic application since  
they can achieve the maximum charge to mass ratio.

5           In one preferred embodiment the invention includes the steps of providing a first solid organic material that is a solid at room temperature (23°C), a second solid organic material that is a solid at room temperature which is substantially different in chemical composition from the first  
10           material, a source of supercritical fluid, a first container having a mechanical agitator and a second container. The first and second organic materials are introduced into the first container along with the supercritical fluid and mechanically agitated. Then, the contents of the first  
15           container are discharged into the second container with the second container maintained at a lower pressure than the first container.

          The first organic material preferably comprises a polymeric resin and the second organic material preferably  
20           comprises a curing agent or a second resin. The supercritical fluid preferably comprises carbon dioxide. As used in the specification and the claims below the terminology "organic material" means any material containing carbon (C) to carbon bonds. Preferably, the first container is substantially free  
25           of any solvent that is capable of dissolving the first or second organic material to any appreciable degree at room temperature (23°C) and pressure (1 atmosphere).

          The foregoing and other features of the invention are hereinafter more fully described and particularly pointed out  
30           in the claims below. The following description sets forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various

5 ways in which the principles of the invention may be employed.

#### Brief Description Of Drawings

In the annexed drawing:

Figure 1 is a schematic view of an apparatus suitable for  
10 use in the present invention.

#### Detailed Description

Referring to Figure 1 there is schematically shown an apparatus 10 for use in practicing applicants' novel invention. More particularly, there is shown a primary  
15 pressure vessel 12 which is connected by piping 13 to a receiver vessel 14. Connected by piping 15 to the pressure vessel 12 is a source of gas 16. Gas 16 is preferably fed under pressure into vessel 12 using a compressor or liquid pump 20. The receiver vessel 14 is connected by piping 17 to  
20 a return tank 22. The return tank 22 is connected by piping 21 to the source of gas 16.

Pressure vessel 12 includes, preferably at its base, a valve 24 for facilitating the emptying of the contents of the pressure vessel 12 into the receiver vessel 14. Included near  
25 the top portion of the pressure vessel 12 is the inlet of piping 32 which is connected to piping 17. Included in piping 32 is a control valve 33. Included in piping 17 is a compressor 34 that serves to compress and transfer gas emanating from the pressure vessel 12 or the receiver vessel  
30 14 into the return tank 22.

5           Pressure vessel 12 includes a sealable opening or access  
port that allows materials to be charged therein and a  
mechanical stirring device 36 for mechanically agitating and  
stirring the contents of pressure vessel 12. Receiving vessel  
14 also includes a sealable opening or access port that allows  
10 materials contained therein to be sampled or removed.  
Preferably, both vessels 12 and 14 are equipped with a quick-  
opening, breech-lock system that requires no hand tools to  
open and close. Also, preferably vessel 12 includes some type  
of valve configuration having a feed port that facilitates the  
15 quick addition of minor amounts of material (e.g., pigments)  
to the vessel 12 once it has been pressurized. Further,  
preferably vessel 14 includes some type of conveyance device  
to facilitate quick unloading of the materials from the  
vessel 14.

20           Pressure vessel 12 and receiving vessel 14 are preferably  
made of stainless steel. However, it will be appreciated that  
any number of alternative materials may be utilized, such as,  
for example, nickel-coated carbon steel or carbon steel  
vessels having other appropriate chemically inert inserts or  
25 liners.

          Apparatus 10 is employed in accordance with the present  
invention by first charging the starting materials for the  
coating powder which one desires to produce into the pressure  
vessel 12. Pressure vessel 12 is then sealed and isolated.  
30 Gas from source 16 is then fed into vessel 12 via piping 15  
until a suitable pressure is attained in vessel 12. A  
critical temperature can be attained by heating vessel 12,  
heating the liquid/gas stream as it enters vessel 12,



5        agitating vessel 12 or combinations thereof. The pressure and  
temperature in vessel 12 converts the gas into a supercritical  
fluid or other suitable process media. Pressure of from about  
350 psi to about 20,000 psi may be utilized. When employing  
a gas such as CO<sub>2</sub>, a pressure of from about 550 psi to about  
10       7000 psi is utilized, and preferably from about 950 psi to  
about 5000 psi, and more preferably from about 1080 psi to  
about 4500 psi is utilized. Of course, it will be appreciated  
that the particular pressure utilized will be a function of  
such variables as the temperature of the vessel 12 and the  
15       particular gas utilized.

Once vessel 12 is pressurized, agitation device 36 is  
then energized and the starting materials and the supercrit-  
ical fluid are then thoroughly mixed. Vessel 12 includes an  
internal temperature of from about -85°C to about 200°C. When  
20       utilizing CO<sub>2</sub>, a temperature from about 15°C to about 160°C is  
employed, and preferably from about 20°C to about 150°C, and  
more preferably from about 31°C to about 100°C. Of course, it  
will be appreciated that the particular temperature utilized  
will be a function of various variables such as, for example,  
25       the gas utilized, the composition of the starting materials,  
pressures employed and equipment configurations. Preferably,  
vessel 12 is held below the melting point of the materials  
being processed, such as, the polymer resins. The temperature  
in vessel 12 preferably is in the range of from about 5  
30       degrees below the T<sub>g</sub> (i.e., glass transition temperature) of  
at least one of the materials being processed up to about the  
melting point of such one material. In the case of an  
amorphous material, "melting point" means the temperature at

5        which the material becomes wholly fluid. It is believed that a supercritical fluid will suppress the T<sub>g</sub> of most materials.

         It will be appreciated that in order to attain the desired temperature in vessel 12, such vessel may be equipped with heat exchangers or other suitable heating/cooling means.

10        The starting materials are mixed in vessel 12 for a period of about 1 to about 480 minutes, preferably 5 to about 300 minutes and more preferably from about 30 to about 240 minutes.

         Once the starting materials have been thoroughly mixed, 15        valve 24 is then opened and maintained in the open position until such time that substantially all of the starting materials originally contained in pressure vessel 12 have been transferred into receiver vessel 14 (which is maintained at a lower pressure than vessel 12). Once substantially all of the 20        starting materials have been transferred, valve 33 is opened in order to depressurize vessel 12 and allow the flow of gas into return tank 22. The gas is then transferred via piping 21 to piping 15 and made available for purposes of reuse.

         While the solid materials are being transferred to 25        receiver vessel 14, vessel 14 is held at preferably a constant and lower pressure than pressure vessel 12. Accordingly, preferably the gas and the starting materials enter receiver vessel 14 at a very high rate. Vessel 14 includes a temperature of from about -85°C to about 220°C, preferably 30        from about -18°C to about 160°C, and more preferably from about 0°C to about 130°C. As with vessel 12, in order to maintain the desired temperature in vessel 14, heat exchangers or other cooling/heating devices may be necessary. Prefera-

5 bly, vessel 14 is held at a temperature below the melting  
point of the materials being processed. Vessel 14 is held at  
a pressure of from about 0 psi to about 5000 psi, preferably,  
from about 100 psi to about 2000 psi, and more preferably from  
about 150 psi to about 1000 psi. Once again, it will be  
10 appreciated that the particular pressure and temperature  
utilized in vessel 14 is a function of various variables, such  
as, for example, the particular gas utilized, the composition  
of the starting materials and equipment configurations.

Preferably, the length of piping 13 is minimized as much  
15 as possible. Disposed in piping 13 just prior to receiver  
vessel 14 is preferably a header 40 that includes multiple  
nozzles through which the gas and/or supercritical fluid and  
starting materials are sprayed. Preferably, header 40 is  
located within receiver vessel 14 or immediately adjacent  
20 receiver vessel 14. Any number of nozzles may be employed to  
spray the material. Of course, it will be appreciated that  
the selection of the proper nozzle will be a function of  
various parameters, such as, for example, the pressures  
employed in vessel 12, the size of particles desired, flow  
25 rates, the materials being processed, and the gas being  
utilized.

The spray nozzles have an orifice opening of from about  
.001" to about 1", preferably from about .005" to about .5"  
and more preferably from about .01" to about .1". Examples of  
30 potential suitable spray nozzles are hydraulic atomizing  
nozzles sold by Spraying Systems Co. of Wheaton, Illinois.

Agitation device 36 comprises an electric motor 50  
driving a mixer 52. Mixer 52 may comprise any number of

5 conventional mixing devices. Of course, it will be appreciated that the selection of the proper mixer will be a function of various parameters, such as, for example, the size of motor  
10 vessel 12. Examples of suitable mixers are Cowles blade mixers sold by Indco, Inc. of New Albany, Indiana. Additional types of mixing blades may also be utilized such as pitched-blade turbine mixers, high-efficiency turbine mixers, disk-style turbine mixers, straight-blade turbine mixers, anchor  
15 impeller mixers and helix impeller mixers. Additionally, more than one mixing blade may be utilized in vessel 12. For example, a pair of spaced turbine impeller mixers turning in opposite directions may be utilized. Additionally, for  
20 example, an anchor-type impeller mixer could be utilized in conjunction with the two turbine impeller mixers. It will be appreciated that the present invention preferably provides for both distributive and dispersive mixing.

The present invention contemplates the use of various process medias (liquids and gases). However, preferably, the  
25 process media is one which is capable of achieving a supercritical state. As used herein and in the claims below the term "supercritical fluid" means a material, that at specific temperatures and pressures, no longer displays the properties of either a gas or a liquid. Examples of potential  
30 supercritical fluids suitable for use with the present invention include, for example, carbon dioxide, water, nitrous oxide, methane, ethane, ethylene, propane, pentane, benzene, methanol, ethanol, isopropanol, various fluorocarbons such as

5 chlorotrifluoromethane and monofluoromethane, toluene,  
pyridine, cyclohexane, decalin, cyclohexanol, o-xylene, and  
tetralin. The critical properties for these compounds are set  
forth below. The present invention contemplates the use of  
these compounds either by themselves or in combination.  
10 Additionally, it will be appreciated that solvents such as,  
for example, acetone, ketones, or ethers may be utilized in  
conjunction with the compounds listed below. However,  
generally, the use of such solvents is not desired.

15	<u>Compound</u>	<u>Critical Temperature (°C)</u>	<u>Critical Pressure (atm)</u>
	CO <sub>2</sub>	31.3	72.9
	H <sub>2</sub> O	374.15	218.3
	N <sub>2</sub> O	36.5	71.7
	Methane	-82.1	45.8
20	Ethane	32.28	48.1
	Ethylene	9.21	49.7
	Propane	96.67	41.9
	Pentane	196.6	33.3
	Benzene	288.9	48.8
25	Methanol	240.5	78.9
	Ethanol	243.0	63.0
	Isopropanol	235.3	47.0
	Isobutanol	275.0	42.4
	Chlorotrifluoro-		
30	methane	28.0	38.7
	Monofluoromethane	44.6	58.0
	Toluene	320.0	40.6
	Pyridine	347.0	55.6
	Cyclohexane	280.0	40.2
35	Decalin	391.0	25.8
	Cyclohexanol	356.0	38.0
	o-Xylene	357.0	35.0
	Tetralin	446.0	34.7

One compound that appears to be particularly well suited  
40 for use with the present invention is carbon dioxide (CO<sub>2</sub>).  
Carbon dioxide is preferred because it is nonflammable,  
reasonably priced, and is easily separated or removed from the  
constituents used in making coating powders at the contemplated  
temperatures and pressures. Therefore, there will be

5 no residual CO<sub>2</sub> in the finished product that could contribute to defects upon application of the coating powder. However, it will be appreciated that the particular gas employed in a particular process will vary depending on such factors as, for example, the availability and cost of the gas, safety  
10 concerns, working pressures and temperatures.

Any number of process medias may be used to produce the coating powders in accordance with the principles of the present invention. However, generally, care must be taken not to utilize starting materials which are soluble in the process  
15 media at operating temperatures and pressures. More particularly, if the starting materials are soluble in the process media, it will not be possible to transfer the starting materials to the receiver vessel 14 without losing starting materials to the process media storage tank 22, which would be  
20 a very undesirable result.

Examples of starting materials suitable for use in the present invention are thermoplastic base resins such as, for example, PVC homopolymer resins, polyamide resins, polyethylene resins, polypropylene resins, cellulose esters, polyester  
25 resins, ethylene-chlorotrifluoroethylene resins, poly(vinylidene fluoride) resins, poly(phenylene sulfide) resins, and thermoset resins, such as, for example, epoxy resins, polyurethane resins, hydroxy and carboxy functional thermoset polyester resins and acrylic resins. Curing agents such as,  
30 for example, dicyanamide type, phenolic formaldehyde, polyamine type, TGIC, beta hydroxy alkyl amide types, tetramethoxymethyl glycoluril and glycidyl functional acrylic resins may also be employed when thermoset base resins are

5 utilized. Flow control agents such as, for example, polyacrylates, silicones, waxes and cellulose acetate butyrate may also be employed. When utilizing thermoplastic resins, plasticizers such as, for example, styrene maleic anhydride and di-butyl thalate may be utilized. Stabilizers such as,  
10 for example, tetrakis(methylene (3,5-di-tert-butyl-hydroxy-hydrocinnamate)) zinc compounds, tin compounds and polyols may also be utilized. Extenders or extender pigments such as, for example, barium sulfate and calcium carbonate may also be utilized. Both organic and inorganic pigments may be included  
15 to impart color, opacity and other visual qualities to the coating produced with the coating powders.

When CO<sub>2</sub> gas is utilized, CO<sub>2</sub> is charged to or utilized in vessel 12 so as to provide from about 10 percent by weight to about 90 percent by weight CO<sub>2</sub> and from about 90 percent by  
20 weight to about 10 percent by weight starting materials, preferably from about 15 percent by weight to about 85 percent by weight CO<sub>2</sub> and from about 85 percent by weight to about 15 percent by weight starting materials, and more preferably from about 20 percent by weight to about 80 percent by weight CO<sub>2</sub>,  
25 and from about 80 percent by weight to about 20 percent by weight starting materials.

Subsequent to processing, the materials in vessel 14 are a collection of homogeneous uniform size particles. In the event any oversize particles or a conglomeration of particles  
30 (foam) are contained in vessel 14, they may be easily milled to the desired size.

By way of illustration and not by any limitation, the following example will describe a method of producing coating

5 powders within the scope of the present invention. Unless  
 otherwise indicated, all parts and percentages are by weight  
 and all temperatures are in degrees Centigrade (°C). For  
 purposes of facilitating a better understanding of the  
 invention, the following example makes reference to the  
 10 various elements of Figure 1.

Example

A mixture of the following starting materials is charged  
 into a pressure vessel 12. Vessel 12 is a 30 gallon stainless  
 steel vessel having an inner diameter of 15 inches.

15	<u>Component</u>	<u>% by Weight</u>
	Resin <sup>1</sup>	56.1
	Stabilizer <sup>2</sup>	.10
	Pigment <sup>3</sup>	1.1
	Curing Agent <sup>4</sup>	4.5
20	Flow Additive <sup>5</sup>	.2
	Extender <sup>6</sup>	38.0

<sup>1</sup>Araldite 3010 Polyester Resin

<sup>2</sup>Anox PP18 Stabilizer

<sup>3</sup>TiO<sub>2</sub>

25 <sup>4</sup>TGIC (Triglycidylisocyanurate)

<sup>5</sup>Polyethylene Homopolymer

<sup>6</sup>Barytes 1-Pfizer (BaSO<sub>4</sub>)

Pressure vessel 12 is then filled with carbon dioxide  
 from source 16 until a pressure of about 2800 psi (80°C) is  
 30 attained within vessel 12 thereby rendering the carbon dioxide  
 a supercritical fluid. The source 16 of carbon dioxide is a  
 standard commercial source maintained at a temperature of  
 about -18°C and a pressure of about 300 psi. Sufficient  
 starting materials are utilized in vessel 12 so as to provide  
 35 in vessel 12 with 70 percent by weight CO<sub>2</sub> and 30 percent by



5 weight starting materials. Once vessel 12 has been properly isolated the materials and supercritical fluid are then mixed for about 60 minutes using agitation device 34. A high torque 30 hp electric motor 50 and a mixer 52 comprising a 6 inch Cowles blade are employed. The mixer is maintained at a depth  
10 of 3 cm from the bottom of pressure vessel 12 and is rotated at a rate of about 750 rpm for thirty minutes. A conventional controlled heating/cooling system is utilized to provide a temperature of about 80°C in vessel 12 during the mixing operation.

15 Upon completion of mixing the starting materials into a homogeneous product, valve 24 is opened and the homogeneous product is then sprayed through header 40 into receiver vessel 14. Receiver vessel 14 is a 120 gallon stainless steel vessel having an inner diameter of about 30 inches. Receiving vessel  
20 14 is maintained at a back pressure of about 300 psi. Piping 13 is about one inch in inner diameter and has a total length of about three inches and header 40 is located within receiver vessel 14. Header 40 includes six separate nozzles arranged in a parallel fashion. The nozzles are hydraulic atomization  
25 nozzles having orifice openings of .02 inches. No temperature control devices are utilized in connection with receiver vessel 14.

Once all of the homogeneous product is transferred to receiver vessel 14, the pressure vessel 12 is fully depressurized of carbon dioxide using piping 30 and compressor 34,  
30 and the carbon dioxide is then transferred to storage tank 22 where it is available for reuse. Pressure vessel 12 is then also available for reuse. Subsequently, the receiver vessel

5        14 is depressurized using piping 17 and compressor 34 and the  
carbon dioxide contained in vessel 14 is transferred to  
storage tank 22 for reuse. The receiver vessel 14 is then  
opened and the homogeneous product is then removed. When  
removed from vessel 14, the homogeneous product comprises  
10        generally a conglomeration of flake-type and rounded particles  
having an average diameter of about 40  $\mu\text{m}$ .

While the invention has been explained in relation to its  
preferred embodiments, it is to be understood that various  
modifications thereof will become apparent to those skilled in  
the art upon reading this specification. Therefore, it is to  
15        be understood that the invention disclosed herein is intended  
to cover such modifications as fall within the scope of the  
appended claims.

5       **What Is Claimed:**

1.   A method of producing coating powders comprising the steps of:

      (A) providing a starting material comprising a first organic material which is solid at room temperature and a second organic material which is solid at room temperature and which is substantially different in chemical composition from such first organic material;

      (B) providing a source of supercritical fluid;

      (C) providing a first container having a mechanical agitator;

      (D) providing a second container;

      (E) introducing such starting material and such supercritical fluid into such first container and mechanically agitating such starting material and such supercritical fluid so as to provide a homogeneous mixture formed by such starting materials; and

      (F) discharging the contents of such first container into such second container so as to collect substantially all of such homogeneous mixture, such second container being maintained at a lower pressure than such first container.

2.   A method as set forth in claim 1 wherein during said step (E) such first container is maintained at a temperature below the melting point of both such first organic material and such second organic material.

5           3. A method as set forth in claim 1 wherein at least a portion of such supercritical fluid is collected from such second container during said step (F) for purposes of reuse.

          4. A method as set forth in claim 1 wherein at least a portion of such supercritical fluid is collected from such  
10 first container for purposes of reuse.

          5. A method of producing a powder blend comprising the steps of:

          (A) providing a first vessel and a second vessel;

          (B) charging such first vessel with starting  
15 materials comprising two or more solid organic components that are solid at room temperature;

          (C) supplying CO<sub>2</sub> gas to such first vessel and holding such CO<sub>2</sub> gas at a temperature in such first vessel of from about 15°C to about 160°C, such that such  
20 first vessel contains from about 10 percent by weight to about 90 percent by weight such CO<sub>2</sub> and from about 10 percent by weight to about 90 percent by weight such starting materials;

          (D) mechanically mixing such starting materials and  
25 such CO<sub>2</sub> in such first vessel; and

          (E) discharging such mixture of such CO<sub>2</sub> and such starting materials from such first vessel into such second vessel, such second vessel being maintained at an internal pressure of from about 0 psi to about 5000 psi  
30 and a temperature of from about -85°C to about 200°C.

          6. A method as set forth in claim 5 wherein after said step (D) such starting materials and such CO<sub>2</sub> are passed through a spray nozzle prior to entering such second vessel.

5           7. A method as set forth in claim 6 wherein such starting materials after said step (E) comprise a foam and such CO<sub>2</sub> is present in such first vessel during said step (D) at a pressure of from about 550 psi to about 7000 psi.

8. A method as set forth in claim 7 further comprising  
10 the step:

(F) of milling such foam contained in such second vessel.

9. A method as set forth in claim 5 wherein such starting materials comprise at least one material selected  
15 from the group consisting of a pigment, filler and extender.

10. A method as set forth in claim 5 wherein during said step (D) such CO<sub>2</sub> gas is held at a temperature of from about 5 degrees below the T<sub>g</sub> of such first organic material up to about the melting point of such first organic material.

20 11. A method as set forth in claim 10 wherein such first organic material comprises a resin and such second organic material comprises a curing agent and during said step (D) the temperature of such CO<sub>2</sub> is such that there is substantially no reaction between such curing agent and such resin.

25 12. A method as set forth in claim 5 wherein during said step (D) such CO<sub>2</sub> is held at a temperature of from about 20°C to about 150°C and a pressure of from about 950 psi to about 5000 psi.

30 13. A method as set forth in claim 5 wherein during said step (D) such CO<sub>2</sub> is held at a pressure of from about 1080 psi to about 4500 psi and a temperature of from about 31°C to about 100°C.

5           14. A method as set forth in claim 5 wherein during said step (E) such second vessel is maintained at a temperature of from about -18°C to about 160°C and a pressure of from about 100 psi to about 2000 psi.

10           15. A method as set forth in claim 5 wherein during said step (E) such second vessel is maintained at a temperature of from about 0°C to about 130°C and a pressure of from about 150 psi to about 1000 psi.

15           16. A method as set forth in claim 5 wherein during said step (D) the temperature and pressure of such CO<sub>2</sub> is such that such CO<sub>2</sub> comprises a supercritical fluid.

          17. A method as set forth in claim 5 wherein during said step (E) such mixture of such starting materials and such CO<sub>2</sub> is passed through a spray nozzle.

20           18. A method as set forth in claim 17 wherein during said step (E) such mixture of such CO<sub>2</sub> and such starting materials is passed through a header comprising multiple spray nozzles arranged in parallel.

          19. A method as set forth in claim 7 wherein such foam comprises a conglomeration of particles.

25           20. A method as set forth in claim 5 wherein during said step (D) such first vessel is substantially free of any solvent that is capable of dissolving such first organic material or said second organic material to any appreciable degree at room temperature and pressure.

30           21. A method as set forth in claim 5 wherein said first organic component is selected from the group consisting of a resin, a curing agent and a stabilizer.

          22. A coating powder produced by the method of:

5 (A) providing a first vessel connected by piping to a second vessel;

(B) charging such first vessel with starting materials;

10 (C) supplying CO<sub>2</sub> gas to such first vessel and holding such CO<sub>2</sub> in such first vessel at such a temperature and pressure such that such CO<sub>2</sub> comprises a supercritical fluid;

15 (D) agitating such supercritical fluid and such CO<sub>2</sub> for a period of from about 1 minute to about 480 minutes; and

(E) transferring such CO<sub>2</sub> and such starting materials through a spray nozzle having an orifice diameter of from about .001" to about 1" and then discharging such CO<sub>2</sub> and such starting materials into such second vessel, such second vessel being maintained at a lower pressure than such first vessel.

20

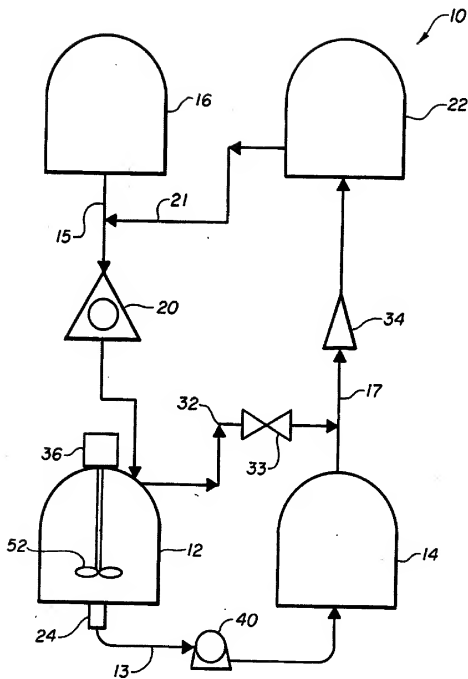


FIG. 1

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/10289

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : B05D 1/00; C08P 6/06; C08J 3/12; C09D 167/02.  
 US CL : 523/307, 340, 342; 521/78, 97; 524/904; 528/501; 239/8.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/307, 340, 342; 521/78, 97; 524/904; 528/501; 239/8.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US, A, 5,027,742 (LEE ET AL) 02 JULY 1991, see col. 2, line 65 to col. 3, line 21, col. 5, lines 7-23, col. 6, lines 45-69, col. 7, lines 1-8, 32-40 and 53-68, col. 8, lines 1-11 and col. 10, line 47 to col. 11, line 40.	1-22 1-22
X Y	US, A, 5,009,367 (NIELSEN) 23 APRIL 1991 see col. 5, lines 6-24 and 58-68, col. 6, lines 1-16, col. 8, line 59 to col. 9, line 50 and col. 15, lines 34-50.	1-22 1-22
Y	US, A, 4,582,731 (SMITH) 15 APRIL 1986 see col. 2, lines 6-37, col. 7, lines 48-65, col. 8, lines 24-45, Abstract and claim 10.	1-22

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special comparison of cited documents:	* Inter document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family

Date of the actual completion of the international search

09 DECEMBER 1993

Date of mailing of the international search report

18 JAN 1994

Name and mailing address of the ISA/US  
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Form PCT/ISA/210 (second sheet)(July 1992)\*

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/10289

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	Water-Borne & Higher Solids Coating Symposium, March 10-12, 1980, (COBBS ET AL), "HIGH SOLIDS COATINGS ABOVE 80% BY VOLUME, pages 176-192, see pages 177-178, 180, 184 (slide 7 and 8) and 186.	<u>1-22</u> 1-22